The numbers representing the specific volumes of the trichlorides of phosphorus, arsenic, and antimony exhibit a gradational order similar to that shown by the volumes of the tetrachlorides of silicon, titanium, and tin, and also by the specific volumes of phosphoryl and vanadyl trichlorides:—

	Mol. weight.	Spec. vol.
PCl_3	137·38	93·54
$AsCl_3$	181·53	94·64
$SbCl_3$	228·68	97·82

although the differences are much less than in the cases of the two latter groups. I intend to return to the question in subsequent communications.

II. "Researches upon the Specific Volumes of Liquids." By T. E. Thorpe, Ph.D., F.R.S.E., Professor of Chemistry in the Yorkshire College of Science, Leeds. Communicated by Prof. A. W. Williamson, For. Sec. R.S. Received February 9, 1876.

III. *On the Specific Volumes of Bromine and Iodine Monochloride, and of Ethene Bromide and Ethene Chloriodide.*

The molecular weight of bromine is, as is well known, nearly equal to the arithmetic mean of the molecular weights of chlorine and iodine: hence the molecular weights of bromine and of iodine monochloride (I Cl) are nearly identical. These substances closely resemble each other in physical properties. Both are dark-red liquids about three times heavier than water. Bromine boils at about 59°·5, and solidifies at $-24°·5$; iodine monochloride melts at $+24°·5$, and boils at 101°: the interval between the boiling- and melting-points of the two compounds is approximately equal.

It appeared to me of interest to determine (1) if the specific volumes of these liquids exhibit a relation similar to that which is shown by their molecular weights, and (2) if the relation in their specific volumes is preserved in analogous combinations of the two bodies. I have accordingly determined the specific gravities, boiling-points, and rates of expansion of bromine and iodine monochloride, and of the compounds which these substances form by their union with ethene, C_2H_4. The observations will also serve to determine if bromine and iodine monochloride preserve, when in combination, the volumes which they possess in the free state.

I. *Bromine.*

About a kilogramme of the purest commercial bromine, dehydrated by agitation with pure and strong sulphuric acid, was carefully distilled, and the fraction boiling at about 60°, which amounted to about two

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to *Proceedings of the Royal Society of London.* www.jstor.org

thirds of the whole, was collected separately. A portion of the distillate was treated with milk of lime and ammonia, and the resulting calcium bromide was tested for iodine in the usual manner, but not a trace was detected. The remainder of the bromine was digested with powdered potassium bromide for several months, again distilled and agitated with phosphoric pentoxide to remove the last traces of moisture. The purified bromine boiled constantly between 59°·6 and 59°·7. $n=0, t'=0$. Barometer (corrected and reduced) 765·2 millims. Reduced and corrected boiling-point 59°·45. In degrees of air-thermometer 59°·27.

A determination of the specific gravity of the bromine gave 3·15787 at 9°·17, compared with water at the same temperature. Its specific gravity at 0°, compared with water at 4°, is 3·18828.

Other observers have found for the specific gravity and boiling-point of bromine:—

	Boiling-point.		Specific gravity.
	°	millims.	
Pierre	63	at 760·02	3·18718 at 0°.
Andrews	58	„ ?	
Bolas and Groves	59·6	„ 751	

The observations of Balard and Löwig are not given, as they were evidently made with bromine containing large quantities of chlorine.

The observations with the dilatometer have led to the following formula as expressing the expansion of bromine between 0° and its boiling-point:—

$$V=1+0{\cdot}001\,062\,18t + 0{\cdot}000\,001\,877\,141t^2 - 0{\cdot}000\,000\,003\,085\,38t^3.$$

By the aid of this formula the following Table has been calculated. It shows the true volume of bromine at every 5° between 0° and 60°, the volume at 0° being taken as 100,000.

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		40	104529	595
5	100536	536	45	105132	603
10	101081	545	50	105742	610
15	101635	554	55	106359	617
20	102197	562	60	106983	624
25	102768	571			
30	103347	579	59°·27	1·069111	
35	103934	587			

The specific gravity of bromine at its boiling-point is 2·98218, and its specific volume $= \frac{2\times 79{\cdot}95^*}{2{\cdot}98218} = 53{\cdot}618$.

---

* Br = 79·95 (Stas).

The rate of expansion of bromine has already been determined by Pierre, who has given the following expression to represent the results of his observations *:—

$$V = 1 + 0{\cdot}001\,038\,186\,255t + 0{\cdot}000\,001\,711\,380\,853t^2 + 0{\cdot}000\,000\,005\,447\,118t^3.$$

This formula gives numbers agreeing fairly well with those afforded by the expression deduced from my determinations, as the following comparison shows (the temperatures are given in degrees of the mercurial thermometer):—

	15°	30°	45°	60°
Pierre........	1·01608	1·03273	1·05068	1·06963
Thorpe	1·01624	1·03326	1·05108	1·06960

Pierre was undoubtedly one of the first to obtain bromine in a state approaching to purity; but it seems probable, in spite of the care which was evidently taken in its preparation, that the sample employed by him in his determination of its rate of expansion was not perfectly free from water. This is indicated by the order of the divergence between the results of our various observations; and the supposition would seem to be confirmed by the high solidifying-point, viz. $-7^{\circ}{\cdot}5$ to -8°, which he observed. Baumhauer has shown that the true freezing-point of bromine is at $-24^{\circ}{\cdot}5$†. Pierre sought to dry his bromine by digestion with calcium chloride. According to Stas, calcium bromide (which, as a desiccating agent is not inferior to the chloride) is incapable of removing the last traces of water from bromine‡.

The specific volume of bromine, calculated from Pierre's numbers, is

$$\frac{159{\cdot}90}{2{\cdot}96881} = 53{\cdot}859.$$

II. *Iodine Monochloride.*

Prepared by heating an intimate mixture of iodine and potassium chlorate, and distilling the product from powdered potassium chlorate,

$$I_2 + 3K\,Cl\,O_3 = K\,Cl\,O_4 + K\,I\,O_3 + K\,Cl + O_2 + I\,Cl.$$

The product was repeatedly distilled in order to break up the last traces of the yellow iodine trichloride which is always formed in slight quantity in the preparation. The liquid ultimately boiled constantly between $99^{\circ}{\cdot}7$ and $100^{\circ}{\cdot}7$; $n=40^{\circ}$, $t'=75^{\circ}$. Corrected and reduced barometer 744·3 millims. Corrected and reduced boiling-point $101^{\circ}{\cdot}3$.

In order to establish its purity the iodine monochloride was analyzed by breaking bulbs containing weighed portions of the liquid under dilute sulphurous acid solution, precipitating the hydrochloric and hydriodic acids by silver nitrate, and digesting the mixed salts with strong nitric acid.

---

* Ann. de Chim. et de Phys. [3] 20.

† Deutsch. Ch. Ges. Ber. 1871, p. 927.

‡ Stas, Nouvelles Recherches sur les Lois des Prop. Chem. &c. Aronstein's German translation, p. 179.

I.	Amount of I Cl taken	1·2482 gram.
II.	" " "	0·5668 "
I.	Silver salts obtained	2·9095 grams.
II.	" " "	1·3223 gram.

From these data, using Stas's numbers for the atomic weights of chlorine, iodine, and silver ($Cl=35{\cdot}46, I=126{\cdot}85, Ag=107{\cdot}93$), we get, by means of the equation

$$W = \frac{I+Ag}{I}x + \frac{Cl+Ag}{Cl}y$$

(in which W = the weight of mixed silver salts, and x and y respectively the amount of iodine and chlorine contained therein), the following results expressed in percentages :—

	I.	II.	Calculated.
Chlorine	21·86	21·98	21·85
Iodine	78·14	78·02	78·15
	100·00	100·00	100·00

Iodine monochloride, as a liquid, bears a marked resemblance to bromine. Although when solidified it melts at a temperature as high as 24°·2 (according to my observations), it not unfrequently remains liquid for many weeks after distillation, and may be cooled to below 0° without congealing. In a freezing-mixture of ice and salt it readily solidifies to a dark reddish-brown crystalline mass. Long-continued shaking at ordinary temperatures occasionally brings about its solidification. A quantity of iodine monochloride which had been liquid for months crystallized in long prisms when subjected to the vibration of a railway-carriage. Mr. J. B. Hannay has already published a number of curious observations on the solidification of this compound *.

The specific gravity of iodine monochloride at 17°·95 is 3·12988, compared with water at 4°; at 0° its specific gravity is 3·18223, compared with water at 4°.

Other observers have found for the melting- and boiling-points of this compound :—

	Boiling-point.	Melting-point.
Schützenberger	100°–102°	30°
Trapp	....	25°
Hannay	100°–102°	24°·7

Observations with the dilatometer have led me to the following formula

---

* Journ. Chem. Soc. 1873, p. 815.

as expressing the expansion of iodine monochloride between 0° and its boiling-point:—

$$V=1+0{\cdot}000\ 915\ 896\ 6t + {\cdot}000\ 000\ 832\ 957\ 6t^2 + 000\ 000\ 002\ 750\ 05t^3,$$

by means of which the following Table has been calculated:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		55	105335	513
5	100460	460	60	105855	520
10	100925	465	65	106381	526
15	101394	469	70	106914	533
20	101867	473	75	107454	540
25	102346	479	80	108001	547
30	102830	484	85	108556	555
35	103320	490	90	109118	562
40	103815	495	100		
45	104315	500			
50	104822	507	101·3	1·104187	

The specific gravity at 101·3 is 2·88196; hence the specific volume of iodine monochloride $= \frac{162{\cdot}31}{2{\cdot}88196} = 56{\cdot}319$.

In the paper already referred to, Mr. Hannay has given the results of a number of observations on the specific gravity of this compound at various temperatures. I am unable to compare his numbers with my own, as the temperatures to which his specific gravities are referred are not given; but the conclusion which Mr. Hannay draws from his observations, "that iodine monochloride expands equally for equal increments of temperature, even near its boiling-point," is obviously erroneous.

III. *Ethene Dibromide*, $C_2H_4Br_2$.

This compound was prepared from well-washed ethene and bromine by means of the arrangement described by Hofmann. The product, after having been dried by phosphorus pentoxide, boiled completely between 130°·1 and 130°·8, the greater portion coming over between 130°·6 and 130°·7; $n=55°$, $t'=110°$. Barometer corrected and reduced 766·6 millims. Corrected and reduced boiling-point 131°·36. In air-thermometer degrees 131°·45.

The statements on record respecting the solidifying-point of this compound are extremely discordant; they vary from −12° or −15° to +13°·1. By careful trial I found that ethene dibromide solidifies at +9°·2, which is almost identical with the number given by Regnault, viz. 9°·53.

The specific gravity of ethene dibromide is 2·19011 at 10°·89, compared with water at 4°. On the supposition that the liquid contracts regularly below its ordinary solidifying-point, its specific gravity at 0° is 2·21324, compared with water at 4°. Other observers have found for the boiling- and freezing-points and specific gravity of this compound:—

	Boiling-point.		Melting-point.	Specific gravity.	
	°		°		°
Regnault ..	131·6	at 760 mm.	9·53		
Pierre	132·6	„ 756·9	13·1	2·16292	at 20·79
Haagen ..	131·6	„ ?	..	2·1827	„ 20
Cahours ..	130	„ ?	0		
Reboul....	..		..	2·198	„ 10

The results of the observations with the dilatometer have afforded me the following formula, which expresses with sufficient exactitude the rate of expansion of this liquid from 0° to its boiling-point:—

$$V = 1+0{\cdot}000\,952\,845t + 0{\cdot}000\,000\,683\,455t^2 + 0{\cdot}000\,000\,00\,394\,763t^3.$$

The following Table is calculated by means of this expression; it shows the true volumes of ethene dibromide at every 5° between 0° and 135°:—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		75	107697	557
5	100478	478	80	108262	565
10	100960	482	85	108835	573
15	101446	486	90	109417	582
20	101936	490	95	110007	590
25	102431	495	100	110607	600
30	102931	500	105	111215	608
35	103436	505	110	111834	619
40	103946	510	115	112462	628
45	104462	516	120	113101	639
50	104984	522	125	113750	649
55	105513	529	130	114409	659
60	106049	536	135	115080	671
65	106591	542			
70	107140	549	131·45	1·14602	

The specific gravity of ethene dibromide at its boiling-point is 1·93124, and its specific volume $= \frac{187{\cdot}90}{1{\cdot}93124} = 97{\cdot}295$.

Pierre, who has already determined the expansion of this liquid, found that a single expression of the form

$$V = 1+at+bt^2+ct^3$$

would not express the results of his observations with sufficient accuracy.

He also selected the volume at 20°·09, the lowest temperature at which he made an observation, as the unit of volume, on the ground that at lower temperatures, particularly in the neighbourhood of its freezing-point, the dilatation of the liquid might be irregular, a supposition which is not confirmed by my observations. He accordingly calculated two expressions of the form *

$$V = 1+a\theta+b\theta^2+c\theta^3,$$

in which $\theta=t-20°·09$.

From 20°·09 to 100°·16 the expansion may be expressed by the formula

$$V=1+0·000\,952\,696\,19\theta + 0·000\,001\,316\,506\,858\theta^2 + 0·000\,000\,001\,062\,687\theta^3\,;$$

and from 100°·16 to 132°·6 by the formula

$$V=1+0·001\,016\,765\,988\theta + 0·000\,000\,102\,231\,770\theta^2 + 0·000\,000\,008\,788\,007\theta^3.$$

These formulæ give results differing but little from those afforded by the expression deduced from my observations, as is evident from the following comparison (the temperatures are given in degrees of the mercurial thermometer):—

	20°·09	50°·09	80°·09	110°·09	130°·09
Pierre....	1·00000	1·02980	1·06213	1·09709	1·12238
Thorpe ..	1·00000	1·03003	1·06230	1·09750	1·12284

The specific volume of ethene dibromide, calculated from the numbers given by Pierre, on the assumption that the specific gravity of the liquid at 20°·79, viz. 2·16292, as given by him, is compared with water at 4° (the temperature of comparison is not stated, but it is probably that which is assumed), is 97·7.

IV. *Ethene Chloriodide*, C_2H_4ICl.

This remarkable compound was first prepared by Maxwell Simpson. To obtain it, finely powdered iodine is suspended in about three times its weight of water, and chlorine is passed into the liquid (which should be kept cool and constantly agitated) until the iodine has nearly disappeared; the liquid is decanted after standing, and a stream of ethene, washed by passing through soda solution, is led into it until both the liquid and the oil which gradually separates out are decolorized. The compound, after washing and drying, is found to boil nearly constantly. When first prepared it is colourless; but on exposure to light it gradually becomes red from the separation of a trace of iodine †.

In order, if possible, to avoid the use of water in the preparation of this compound, I attempted to obtain it by the direct addition of pure iodine monochloride to ethene, matters being so arranged that a large excess of the hydrocarbon was present during the reaction. The result was altogether different from what I anticipated. When the two substances are brought together, nearly the whole of the iodine is set free, and Dutch liquid is formed, only a very small quantity of the chloriodide being produced: I varied the conditions of the experiment in several ways, but with invariably the same result. I have since found that Geuther has made the same observation *. It is remarkable that the presence of water should so completely modify the reaction. It must be remembered, however, that in an aqueous solution of iodine chloride there is always more or less free hydrochloric acid and iodic acid, a portion of the iodine chloride being decomposed in accordance with the equation

---

* *Loc. cit.*

† Proc. Roy. Soc. xi. p. 590, xii. p. 278.

$$5ICl + 3H_2O = 5HCl + HIO_3 + 2I_2,$$

the extent of the decomposition being probably dependent on the ratio of the products of decomposition to the compound still undecomposed. This supposition is rendered probable by the observations of Hannay, that, on filtering the solution from the iodine, a further precipitation gradually occurs; and that on mixing an aqueous solution of iodine chloride with carbon bisulphide, which dissolves the iodine as it separates out, the whole of the compound is gradually decomposed, nothing but iodic and hydrochloric acids being left in the water.

Dr. Maxwell Simpson kindly sent me a sample of ethene chloriodide prepared by the process above described, with the direction that in order to render it quite pure it was merely necessary to wash it with dilute potash and dry it. After being dried over phosphorus pentoxide it boiled almost completely between 139°·1 and 140°·1. Barometer 759·3 millims.; $n=50°$, $t'=110°$; corrected and reduced boiling-point 140°·1.

Two observations of specific gravity gave, (1) 2·13363 at 15°·28 and (2) 2·13329 at 15°·43, compared with water at 4°. Reduced to 0°, the specific gravity becomes (1) 2·16440 and (2) 2·16437. Mean 2·16439, compared with water at 4°.

Ethene chloriodide solidifies to a white crystalline mass in a mixture of snow and hydrochloric acid.

Other observers have found:—

	Boiling-point. ° °	Barometer. millims.	Specific gravity.		°
Simpson......	140–143	..	2·151	at	0
Maumené	146	753	2·39	„	20

Observations with the dilatometer have led to the formula

$$V = 1+0{\cdot}000\,936\,917\,6\,t + 0{\cdot}000\,000\,415\,129\,t^2 + 0{\cdot}000\,000\,004\,501\,4\,t^3,$$

which represents with sufficient accuracy the expansion of ethene chlor-

---

* Jahresbericht &c. vol. xv. p. 491.

iodide between 0° and its boiling-point. The following Table gives the true volume of this liquid for every 5° between these intervals :—

° C.	Volume.	Diff.	° C.	Volume.	Diff.
0	100000		85	108541	549
5	100470	470	90	109097	556
10	100942	472	95	109661	564
15	101416	474	100	110234	573
20	101894	478	105	110816	582
25	102375	481	110	111408	592
30	102860	485	115	112009	601
35	103349	489	120	112619	610
40	103843	494	125	113239	620
45	104341	498	130	113871	632
50	104845	504	135	114513	642
55	105354	509	140	115166	653
60	105868	514	145	115830	664
65	106389	521			
70	106916	527	140·1	1·15179	
75	107450	534			
80	107992	542			

The specific gravity of ethene chloriodide at its boiling-point is 1·87915; and its specific volume $= \frac{190\cdot31}{1\cdot87915} = 101\cdot27$.

It is evident from these observations that the specific volumes of bromine and iodine chloride are not equal, neither are the specific volumes of ethene bromide and ethene chloriodide; the bodies with the greater molecular weights have the greater specific volumes.

	Molecular weight.	Specific volume.
Bromine	159·90	53·62
Iodine chloride	162·31	56·32
Ethene bromide	187·90	97·30
Ethene chloriodide	190·31	101·27

The number obtained for iodine monochloride differs considerably from the volume calculated by means of Kopp's values (Cl = 22·8, I = 37·5), viz. 60·3. The specific volume of bromine (Br_2) is also less than Kopp's number, 55·6. The value assigned to chlorine is unquestionably far more accurate than that given to iodine, since the value of the latter element was calculated from only two or three compounds, whereas the former value was deduced from a comparatively large number of chlorinated products. That the value for iodine needs revision seems to be confirmed by Billet's observations of the specific gravities of liquid iodine at various temperatures. His results are[*]:—

Temperature ..	107°·0	111°·7	124°·3	133°·5	151°·0	170°·0
Specific gravity	4·004	3·988	3·944	3·918	3·866	3·796

If these numbers be plotted down and the curve prolonged to the boiling-point of iodine, we find that the specific gravity of iodine at this temperature is 3·780; hence the specific volume of iodine (I)

$$= \frac{126{\cdot}85}{3{\cdot}780} = 33{\cdot}5.$$

If now this value be added to that of chlorine, as given by Kopp, we get a result identical with the observed volume of iodine monochloride—

$$33{\cdot}5 + 22{\cdot}8 = 56{\cdot}3.$$

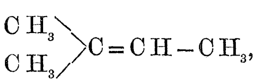
If we subtract the specific volumes of C_2H_4, as calculated by the aid of Kopp's values ($C=11$, $H=5{\cdot}5$, $C_2H_4=44$), from the specific volumes of ethene bromide and ethene chloriodide, we obtain numbers which are nearly equal to the specific volumes of bromine and iodine chloride respectively:—

$$97{\cdot}30 - 44 = 53{\cdot}30.$$
$$101{\cdot}27 - 44 = 57{\cdot}27.$$

This correspondence between the two sets of values seems to warrant the conclusion that bromine and iodine chloride possess the same volume in a compound which they have when in the free state.

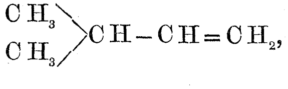
In order to ascertain how far this conclusion is general, I purpose to determine the specific volumes of such of the C_5H_{10} hydrocarbons as I can obtain in quantity and of sufficient purity, and also of the specific volumes of their combinations with bromine. Buff has already made observations upon amylene; but a recently published investigation by Flavitzky has rendered it probable that the preparation employed by Buff was a mixture of isopropylethene and trimethylethene[†].

According to Flavitzky the olefine boiling at 35° is trimethylethene,



$$\left.\begin{array}{l} CH_3 \diagdown \\ CH_3 \diagup \end{array}\right\rangle C=CH-CH_3,$$

and not isopropylethene,



$$\left.\begin{array}{l} CH_3 \diagdown \\ CH_3 \diagup \end{array}\right\rangle CH-CH=CH_2,$$

which boils at 25°: both hydrocarbons are derivable from fermentation amyl-alcohol.

---

[*] Jahresbericht &c. vol. viii. p. 46.

[†] Ann. der Chem. u. Pharm. vol. clxxix. p. 340.

Since bromine and iodine chloride appear to have the same volume in union with ethene that they have when uncombined, it is not unreasonable to suppose that the same may be true of ethene itself, viz. that at its boiling-point it would possess the same volume which it has in the bromide and chloriodide at their respective boiling-points. On this assumption the specific gravity of liquid ethene would be—

Calculated from	$C_2H_4Br_2$........	0·641
„ „	C_2H_4ICl........	0·624

III. "Experimental Contributions to the Theory of Electrolysis." By ALFRED TRIBE, Lecturer on Chemistry in Dulwich College. Communicated by J. H. GLADSTONE, Ph.D., Fullerian Professor of Chemistry in the Royal Institution. Received January 13, 1876.

In July 1800 Nicholson and Carlisle first effected the decomposition of water by the pile of Volta; and they were not a little surprised when the constituent gases of the water appeared separately at some considerable distance from each other[*], but they offered no opinion as to the cause of so singular a phenomenon. A little later Cruickshank also decomposed water by the pile, and, for the first time, many metallic salts[†]. He also, like Nicholson and Carlisle, was much struck by the appearance of the compounds round poles separated some distance, and attempted to explain the phenomenon by supposing that the principle of galvanism could exist in an oxygenated and deoxygenated condition—that in entering water at the negative end, it combined with oxygen, liberating hydrogen, and that on arriving at the positive end the oxygen either escaped or combined with the wire[‡].

This hypothesis, which involves the idea of an imponderable capable of combining with ponderables, underwent various modifications by Fourcroy and Vauquelin and Thenard, and by Dr. Bostock and others.

But the next step of importance to the theory of electrolysis was the idea of the passage into or through the liquid of one or both constituents of the electrolyte, which was first roughly foreshadowed by an anonymous correspondent of Nicholson's Journal (vol. iv. p. 472), and which was thus more explicitly expressed in 1807 by Sir H. Davy:—"The oxygen of a portion of water is attracted by the positive surface at the same time that the other constituent part, the hydrogen, is repelled by it, and the opposite process takes place at the negative surface; and in the

---

[*] Nicholson's Journal, Old Series, vol. iv. p. 183.

[†] *Ibid.* p. 189.

[‡] *Ibid.* New Series, vol. iii. p. 9.